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Molecular constants of some dihaloboranes

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A fresh study of molecular potential constants, generalized mean square amplitudes, Coriolis coupling constants and centrifugal distortion constants has been attempted here in ten dihaloborane molecules. The values of all these molecular constants, obtained on the basis of kinetic constants, are found to be very reasonable in the light of the results available in the literature.

1. Introduction

Molecular kinetic constants have been employed by several authors (Thirugnanasambandam *et al* 1969, 1974a, 1974b, 1975a 1975b, 1975c, 1975d, 1975e; Sanyal *et al* 1972, 1973, 1947a, 1974b, 1975; Srivastava *et al* 1972; Sharma *et al* 1975) to obtain acceptable sets of potential constants in different types of polyatomic molecules involving 2×2 as well as 3×3 vibrational problems. This new procedure has led to significant results not only regarding the potential constants but also other types of molecular constants such as mean amplitudes of vibration, shrinkage effects, Coriolis coupling constants and centrifugal distortion constants in different types of molecules. The calculated values of these molecular constants are found to be in very good agreement with the corresponding observed values, thus establishing the merits of the new procedure involving kinetic constants (Thirugnanasambandam *et al* 1975d, 1975e).

The purpose of the present paper is to study the molecular constants of ten dihaloborane molecules on the basis of Wilson's FG matrix method, simplified with the help of kinetic constants.

2. Molecular Constants

The symmetry coordinates used in the present investigation are essentially the same as those used by Oka and Morino (1963) and Ford & Orville-Thomas (1967). The general expressions relating to the F matrix elements and the kinetic constants in this type of molecules have already been reported in the paper on some planar symmetrical XYZ_2 molecules and ions (Thirugnanasambandam *et al* 1975d). The generalized mean square amplitudes and Coriolis coupling constants have been calculated following the methods of Morino & Hirota (1955) and Meal & Polo (1956) respectively. The centrifugal distortion constants have been obtained following the method developed by Cyvin *et al* (1968, 1970).

3. Results and Discussion

The structural parameters and the vibrational frequencies employed in the present investigation of molecular constants are given in table 1.

(a) *Kinetic constants and potential constants :* The molecular kinetic constants and the potential constants of the dihaloboranes are presented in tables 2 and 3 respectively. It is interesting to note the bond-opposite angle interaction potential constants $f_{D\alpha}$ and $f'_{D\beta}$ as well as the corresponding kinetic constants $k_{D\alpha}$ and $k'_{D\beta}$ are negative in all these molecules. Similar behaviour has already been noticed in the case of formaldehyde molecules, formate ions, carbonyl and thiocarbonyl halides (Thirugnanasambandam *et al* 1975d). The characteristic stretching potential constant f_D relating to the $B—H$ or $B—D$ bond remains largely the same in these molecules. It may be seen that the boron-halogen stretching potential constant and indeed almost all the potential constants in dihaloboranes show uniform variations, decreasing with decreasing electronegativity of the halogen atoms.

(b) *Mean Amplitudes of vibration* : The generalized mean square amplitudes of the various bonded and nonbonded distances are given in table 4. It may be seen from this table that ^{10}B - ^{11}B isotope effects are not very large, but that the mean amplitudes of the bonded atom pairs in the ^{10}B compounds are generally larger than those in the ^{11}B compounds. Similarly the $(X—Y)$ and $(Y\,..\,Z)$ amplitudes of the dihaloborane molecules are considerably larger than those in the corresponding deuterated compounds. Moreover, the bonded $X—Z$ and nonbonded $Y\,..\,Z$ and $Z\,..\,Z$ vibrational amplitudes increase uniformly with the increasing mass of the halogen atom in these molecules. The present values of the vibrational amplitudes compare well with those reported by Venkateswarlu and Purushothaman (966) for $^{11}BHCl_2$ and $^{11}BHBr_2$ molecules.

(c) *Coriolis coupling constants and centrifugual distortion constants :* The calculated values of the Coriolis coupling constants and the centrifugal distortion constants are given in Tables 5 and 6 respectively. The zeta values are found to obey the relevant sum rules very well. No experimental data is available for comparison with regard to these molecules except in the case of the difluoroborane molecule for which the experimental values of the centrifugal distortion parameters have been reported by Kasuya *et al* (1968). A comparison of the present values of the centrifugal distortion constants with the experimentally observed values is brought out in table 7. The close fit of the present values with the corresponding observed values bring out the significance of the method of kinetic constants adopted in the present investigation of molecular constants.

It may be added that the following calculations, hitherto unavailable in the literature, have been reported here for the first time : (i) the generalized mean square amplitudes of BHF_2 and BDX_2 (X = F, Cl, Br), (ii) Coriolis coupling

Table 1. Structural parameters and vibrational frequencies

S. No.	Molecule	D(Å)	d(Å)	β	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(B_1)$	$\nu_5(B_1)$	$\nu_6(B_2)$	Reference
							(cm^{-1})				
1.	$^{10}BHF_2$	1.189	1.311	120°51	2619	1193	555	1506	1346	945	a, b, c
2.	$^{11}BHF_2$	...	..	...	2619	1162	550	1461	1402	924	a, c
3.	$^{10}BDF_2$	.	...	.	1959	1147	551	1419	1199	807	a, c, d
4.	$^{11}BDF_2$	..	..		1959	1125	544	1394	1195	787	a, c
5.	$^{10}BHCl_2$	1.20	1.70	120°	2617	762	289	1109	860	795	e, f
6.	$^{11}BHCl_2$	.	.		2607	740	287	1089	892	784	e, f
7.	$^{10}BDCl_2$	..			1969	735	288	1050	641	661	e, f
8.	$^{11}BDCl_2$	.	.		1902	714	285	1005	640	645	e, f
9.	$^{11}BHBr_2$	1.22	1.87	120°	2622	595	183	1036	772	731	e, g
10.	$^{11}BDBr_2$	...	...	.	1960	585	183	870	656	625	e, g

a : Kasuya *et al* (1968). b : Lynds *et al* (1965b). c : Lynds (1965). : d : Perec *et al* (1965). e : Brieux de Mandirola *et al* (1964 65). f : Bass *et al* (1964). g : Lynds *et al* (1965a).

Table 2. Kinetic constants (10^{-23}g)

S. No.	Molecule	k_D	k_1	k_{D1}	k_{1d}	k_α	k_β	$-k_{D\alpha}$	$k_{d\alpha}$	$-k'_{d\beta}$	k_δ
1.	$^{10}BHF_2$	0.1639	1.7325	0.0333	0.7790	0.3005	0.1180	0.0371	0.3588	0.2348	0.0818
2.	$^{11}BHF_2$	0.1640	1.7655	0.0326	0 7588	0.3085	0.1203	0.0364	0.3517	0.2300	0.0850
3.	$^{10}BDF_2$	0.3210	1.7918	0.0651	0 7327	0.3086	0 1506	0.0727	0.3516	0.2711	0.1120
4.	$^{11}BDF_2$	0.3212	1.8222	0.0639	0.7146	0.3162	0.1529	0.0713	0.3448	0.2655	0.1181
5.	$^{10}BHCl_2$	0.1653	2.8109	0.0361	1 7413	0.4543	0.1894	0.0417	0.7240	0.4753	0.0732
6.	$^{11}BHCl_2$	0.1653	2.8547	0.0357	1.7129	0.4645	0.1930	0.0412	0.7152	0.4694	0.0757
7.	$^{10}BDCl_2$	0.3262	2.8831	0.0713	1.6844	0.4646	0.2195	0.0824	0.7151	0.5114	0.1060
8.	$^{11}BDCl_2$	0.3263	2.9248	0.0705	1.6577	0.4745	0.2231	0.0814	0.7065	0.5050	0.1113
9.	$^{11}BHBr_2$	0.1664	5.6684	0.0389	4.3917	0.8825	0.3650	0.0449	1.7576	1.1346	0.0729
10.	$^{11}BDBr_2$	0.3305	5.7553	0.0772	4.3226	0.8945	0.3956	0.0892	1.7473	1.1732	0.1094

Table 3. Potential constants (10^5 dynes cm^{-1})

S. No.	Molecule	f_D	f_d	f_{Dd}	f_{dd}	f_τ	f_β	$-f_{D_2}$	f_{d_2}	$-f'_{d\beta}$	f_δ
1.	$^{10}BHF_2$	3.6976	8.3997	0.1235	0.9258	0.3284	0.3166	0.0406	0.3922	0.5044	0.2593
2.	$^{11}BHF_2$	3.7309	8.3461	0.1180	0.7915	0.3311	0.3369	0.0391	0.3775	0.5142	0.2577
3.	$^{10}BDF_2$	3.7811	8.0617	0.2328	0.9613	0.3324	0.4258	0.0783	0.3788	0.6400	0.2588
4.	$^{11}BDF_2$	3.8474	8.0665	0.2239	0.8276	0.3320	0.4244	0.0748	0.3620	0.6182	0.2595
5.	$^{10}BHCl_2$	3.6867	4.8418	0.0423	0.4815	0.1346	0.1224	0.0124	0.2145	0.2444	0.1641
6.	$^{11}BHCl_2$	3.6912	4.9339	0.0410	0.3156	0.1357	0.1285	0.0121	0.2090	0.2480	0.1650
7.	$^{10}BDCl_2$	3.8050	4.6288	0.0816	0.5972	0.1367	0.1286	0.0242	0.2104	0.2504	0.1643
8.	$^{11}BDCl_2$	3.6099	4.5568	0.0788	0.5693	0.1367	0.1284	0.0235	0.2036	0.2441	0.1645
9.	$^{11}BHBr_2$	3.7307	4.6370	0.0181	0.0492	0.1049	0.0970	0.0053	0.2090	0.2279	0.1385
10.	$^{11}BDBr_2$	3.8215	4.1375	0.0368	0.6579	0.1063	0.1214	0.0106	0.2076	0.2684	0.1517

Table 4. Generalized mean square amplitudes (10^{-3} Å^2) at 298.16K

S. No	Molecule	Distance	$<\Delta z^2>$	$<\Delta x^2>$	$<\Delta y^2>$	$<\Delta z\,\Delta x>$
1.	$^{10}BHF_2$	B-H	7.0384	13.2943	15.9381	0
		B-F	1.8432	2.8665	1.0333	−0.0940
		H . . F	9.0271	11.6437	8.8548	1.8013
		F . . F	2.8284	0.1476	0	0
2.	$^{11}BHF_2$	B-H	6.9780	12.7115	16.3135	0
		B-F	1.7906	2.7653	0.9367	−0.0893
		H . . F	9.4508	11.2850	9.4320	1.6120
		F . . F	2.8369	0.1521	0	0
3.	$^{10}BDF_2$	B-D	5.1607	7.9237	9.6673	0
		B-F	1.9235	2.8790	1.6884	−0.0618
		D . . F	6.5776	6.9904	3.2754	0.4083
		F . . F	2.8392	0.2249	0	0
4.	$^{11}BDF_2$	B-D	5.0758	7.8543	9.8261	0
		B-F	1.8514	2.7905	1.5600	−0.0635
		D . . F	6.5571	7.0016	3.5558	0.4411
		F . .F	2.8624	0.2305	0	0
5.	$^{10}BHCl_2$	B-H	7.0398	21.5105	21.0188	0
		B-Cl	2.2508	5.2587	0.9420	−0.2631
		H . . Cl	13.2817	18.2606	13.0613	4.5718
		Cl . . Cl	4.3055	0.0613	0	0
6.	$^{11}BHCl_2$	B-H	7.0022	20.5755	21.3184	0
		B-Cl	2.1428	5.1239	0.8317	−0.2683
		H . . Cl	12.9696	17.7261	13.7288	4.2306
		Cl . . Cl	4.3226	0.0632	0	0
7.	$^{10}BDCl_2$	B-D	5.1208	15.8625	13.6257	0
		B-Cl	2.3234	5.2304	1.7078	−0.2128
		D.Cl	9.9266	13.4396	5.6857	2.9357
		Cl.Cl	4.3120	0.1082	0	0
8.	$^{11}BDCl_2$	B-D	5.2191	15.8207	13.9048	0
		B-Cl	2.2655	5.0913	1.5545	−0.2028
		D.Cl	9.9978	13.4659	6.1611	2.9423
		Cl.Cl	4.3068	0.1123	0	0
9.	$^{11}BHBr_2$	B-H	6.9672	24.2130	23.7763	0
		B-Br	2.0962	6.5435	0.7799	−0.5081
		H . . Br	14.6967	20.9790	15.9437	5.3339
		Br . . Br	4.7961	0.0147	0	0
10.	$^{11}BDBr_2$	B-D	5.0646	15.6670	14.9692	0
		B-Br	2.3320	6.4784	1.4229	−0.3257
		D. . Br	10.0678	14.3850	7.1618	2.2090
		Br . . Br	4.7463	0.0248	0	0

Table 5 Coriolis coupling constants

S. No.	Molecule	$-\zeta_{16}^{x}$	ζ_{26}^{y}	$-\zeta_{36}^{z}$	$-\zeta_{14}^{y}$ ζ_{15}^{y}	ζ_{24}^{y} ζ_{25}^{y}	$-\zeta_{34}^{y}$ $-\zeta_{35}^{y}$	$-\zeta_{46}^{z}$	ζ_{56}^{z}
1.	$^{10}BHF_2$	0.9058	0.3203	0.2773	0.2776 0.9523	0.5555 0.0511	0.7838 0.3011	0.6468	0.7627
2.	$^{11}BHF_2$	0.9070	0.3154	0.2790	0.2602 0.9566	0.5395 0.0313	0.8008 0.2898	0.6296	0.7770
3.	$^{10}BDF_2$	0.8939	0.3136	0.3202	0.3957 0.9093	0.4950 0.9330	0.7735 0.4056	0.7567	0.6538
4.	$^{11}BDF_2$	0.8903	0.3191	0.3248	0.3702 0.9183	0.4873 0.0632	0.7909 0.3908	0.7420	0.6705
5.	$^{10}BHCl_2$	0.9372	0.2894	0.1947	0.2882 0.9544	0.6795 0.1460	0.6748 0.2607	0.5981	0.8014
6.	$^{11}BHCl_2$	0.9393	0.2818	0.1958	0.2728 0.9587	0.6661 0.1282	0.6942 0.2538	0.5799	0.8147
7.	$^{10}BDCl_2$	0.9209	0.3135	0.2317	0.3998 0.9120	0.6285 0.2000	0.6673 0.3581	0.7198	0.6942
8.	$^{11}BDCl_2$	0.9215	0.3093	0.2349	0.3801 0.9201	0.6195 0.1777	0.6868 0.3489	0.7032	0.7110
9.	$^{11}BHBr_2$	0.9507	0.2796	0.1340	0.2865 0.9567	0.7982 0.2096	0.5298 0.2017	0.5667	0.8240
10.	$^{11}BDBr_2$	0.9355	0.3135	0.1631	0.3986 0.9152	0.7511 0.2888	0.5263 0.2810	0.6942	0.7198

Table 6. Centrifugal distortion constants (MHz)

S. No.	Molecule	$-\tau_{aaaa}$	$-\tau_{bbbb}$	τ_{aabb}	$-\tau_{abab}$
1.	$^{10}BHF_2$	11.60715	0.04663	0.45785	0.06546
2.	$^{11}BHF_2$	10.98643	0.04684	0.44198	0.06247
3.	$^{10}BDF_2$	4.05128	0.04682	0.25701	0.05452
4.	$^{11}BDF_2$	3.96796	0.04736	0.25595	0.05368
5.	$^{10}BHCl_2$	9.20982	0.00594	0.16647	0.00943
6.	$^{11}BHCl_2$	8.46597	0.00593	0.15841	0.00866
7.	$^{10}BDCl_2$	3.60638	0.00589	0.10276	0.01132
8	$^{11}BDCl_2$	3.55212	0.00593	0.10049	0.01097
9.	$^{11}BHBr_2$	6.52016	0.00081	0.05415	0.00114
10.	$^{11}BDBr_2$	2.84223	0.00081	0.03545	0.00131

Table 7. Comparison of centrifugal distortion constants (MHz)*

S. No.	Molecule	$-d_J$	$-d_K$	$-d_{JK}$	$d_{EJ}(10^{-6})$	$d_{EK}(10^{-5})$	Ref.
1.	$^{10}BHF_2$	0.0408	3.6131	1.4681	5.16	9.87	pw
		0.048		0.89	5.83	3.76	
		±0.002		±0.04	±0.36	+0.25	a
2	$^{11}BHF_2$	0.0419	3.0435	1.3722	5.11	9.16	pw
		0.0176	--	0.87	5.86	3.80	
		±0.009		±0.02	±0.18	±0.14	a
3	$^{10}BDF_2$	0.0346	1.4131	0.8085	4.41	5.604	pw
		0.045	--	0.545	5.20	2.22	
		±0.002		±0.009	±0.30	±0.06	a
4.	$^{11}BDF_2$	0.0346	1.2778	0.7824	4.43	5.393	pw
		0.0386	2.96	1.134	4.91	8.95	
		±0.0003	±0.10	±0.020	±0.07	±0.22	a

*The constants d_{EJ} and d_{EK} are dimensionless
a = Kasuya *et al* (1968)

constants of BDX_2 (X = Cl, Br) and (iii) the centrifugal distortion constants of $BH(D)X_2$ (X = Cl, Br).

4. Conclusion

A fresh attempt has been made here to evaluate all the general valence force constants, generalized mean square amplitudes, Coriolis coupling constants and centrifugal distortion constants of ten dihaloborane molecules. The values of all these molecular constants, obtained here on the basis of the method of kinetic constants, appear to be highly reasonable showing the importance of the kinetic constants in molecular vibrations.

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